ChE-304 Problem Set 3

Week 3

Problem 1

A change in entropy for an ideal gas system undergoing a change in entropy where both, T, V and P can be calculated with:

$$\Delta S = n\left(C_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)\right)$$

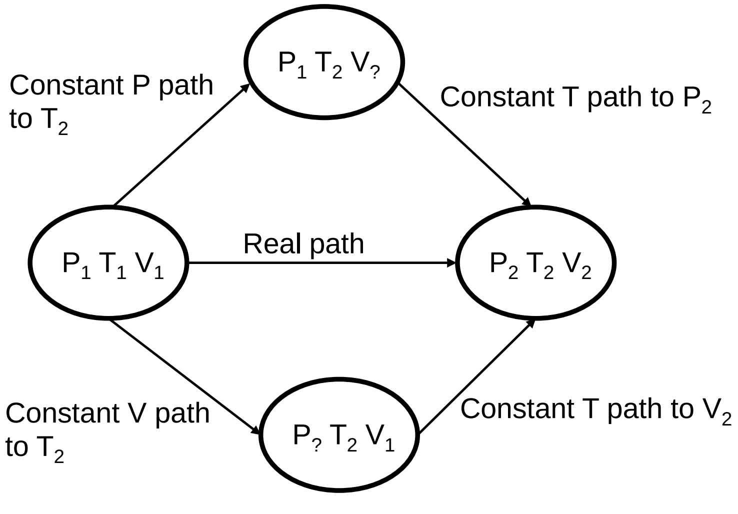
or

$$\Delta S = n\left(C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)\right)$$

Prove that these expressions hold for a single change where both T, V and P are changing starting from the definition of ΔS: $\Delta S = \int \frac{dQ_{rev}}{T}$

Solution

S is a state function. Therefore, ΔS only depends on the initial and final state not on the path taken. Therefore, even if T, P and V are changing at once, we can choose a virtual path for which it is easier to calculate ΔS:



Let's start with the constant P path:

$$\Delta S = \int \frac{dQ_{rev}}{T}$$

$dU = dQ_{rev} + dW_{rev} = nC_V dT$ (for an ideal gas)

$dW_{rev} = -PdV$ We add a negative sign because for a positive dV, the system "loses" work

$dW_{rev} = -P_1 dV = -P_1 d\left(\frac{nRT}{P_1}\right) = -nRdT$ (the last step is only "allowed" at cst P)

$$dQ_{rev} = dU - dW_{rev} = nC_V dT + nRdT = nC_P dT$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{nC_P dT}{T} = nC_P \ln\left(\frac{T_2}{T_1}\right)$$

Note that because we are at constant P, we can also write: $\Delta S = nC_P \ln\left(\frac{V_2}{V_1}\right)$

Now, we do a constant T change:

$$dU = nC_V dT = 0 \rightarrow dQ_{rev} = -dW_{rev} = pdV = \frac{nRT}{V} dV$$

Again, above we have: $dW_{rev} = -PdV$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{PdV}{T} = nR \int \frac{pd(T_2/P)}{T_2} = nR \int -\frac{PdP}{P^2} = -nR \ln\left(\frac{P_2}{P_1}\right)$$

Therefore: $\Delta S_{tot} = nC_P \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{P_2}{P_1}\right)$

Now, let's take the other path (constant V first):

$$dQ_{rev} = dU - dW_{rev} = nC_V dT + PdV = nC_V dT$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{nC_V dT}{T} = nC_V \ln\left(\frac{T_2}{T_1}\right)$$

The second step is the same as before (Cst T):

$$dQ_{rev} = -dW_{rev} = PdV = \frac{nRT}{V} dV$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{pdV}{T} = nR \int \frac{T_2 dV}{V\,T_2} = nR \ln\left(\frac{V_2}{V_1}\right)$$

Therefore, we find the alternate expression:

$$\Delta S_{tot} = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

Problem 2

A community (average T=27°C) has an enormous underground reservoir of high-pressure (inert) gas. The reservoir has the following properties:

T= 237 °C
P = 9.95 atm
V= 10^6 m^3
Depth = 2000 m below the surface
Cp = 36 J/(mol K)
Mw= 0.03 kg/mol

Assume that the gas is ideal.

What is the maximum amount of work that the community could extract out of the gas?

Solution:

For a batch system:

$$W_{Ex,1\to 0} = -\left(U_0 - \left(U + E_p + E_k\right)_1\right) + T_0(S_0 - S_1) - p_0(V_0 - V_1)$$

We can ignore E_k but not E_p! And we know what ΔU is for an ideal gas:
$W_{Ex,1\to 0} = \Delta U + E_p + T_0\Delta S - p_0(V_0 - V_1) = nC_V\Delta T + E_p + T_0\Delta S - p_0(V_0 - V_1)$

For an ideal gas: $C_V = C_P - R = 36 - 8.314 = 27.69\, J/(mol\ K)$

ΔS for an ideal gas when both T and P are changing:

$$\Delta S = n\left(C_p \ln\left(\frac{T_0}{T_1}\right) - R\ln\left(\frac{P_0}{P_1}\right)\right)$$

$$m = n\ Mw = \frac{PV}{RT} Mw = 9.95 * 101325 \frac{10^6}{8.314\ \ 510}\ 0.03 = 7.13\ 10^6 kg$$

$$\Delta S = \frac{7.13\ 10^6}{0.03}\left(36 \ln\left(\frac{300}{510}\right) - R\ln\left(\frac{1}{9.95}\right)\right) = -1.42\ 10^5 J/K$$

$$E_p = mg\Delta z = 7.13\ 10^6 * 9.8\ (-2000) = -1.40\ 10^{11}\ J$$

$$\Delta U = nC_v\Delta T = \frac{7.13\ 10^6}{0.03}\ 27.69\ * 210 = 1.38\ 10^{12}\ J$$

$W_{Ex,1\rightarrow 0} = 1.38\ 10^{12}\ J - 1.40\ 10^{11}\ J - 300K * 1.42\frac{10^5 J}{K} - 101325\left(10^6 * \frac{9.95}{1}\frac{300}{510} -\right.$

$\left.10^6\right) = 7.53^{11}\ J$

Problem 3

When you heat your house with fuel oil (“mazout”) you produce gases in a continuous process in the burner that are around 1400 °C (1673 K). These gases are ultimately cooled to around 100°C in order to heat a home at a temperature that is generally constant at around 20°C (and no work is produced in the process). This is not efficient because a tremendous amount of work/exergy is wasted by not exploiting this temperature difference. Can you calculate the maximum amount of work that is lost as a fraction of the heat used to heat the house?

The gases can be considered ideal and they are always at a pressure of 1 atm (101’325 Pa).

The Cp can be assumed to be independent of temperature and equal to:

Cp= 30 J/(mol K) (assumed to be constant with T°)

Solution:

We calculate the exergy of the gas going from 1400°C to 100°C

$$W_{ex,1\to 2} = -(H_2 - H_1) + T_0(S_2 - S_1)$$

With a constant Cp:

$$\Delta H = Cp\Delta T = -30 * 1300 = -39'000\,J$$

For a constant P path:

$$dQ_{rev} = dU - dW_{rev} = nC_V dT + nRdT = nC_P dT$$

$$\Delta S = \int \frac{dQ_{rev}}{T} = \int \frac{nC_P dT}{T} = nC_P \ln\left(\frac{T_2}{T_1}\right)$$

$$= 30 * \ln\left(\frac{373}{1673}\right) = -45\,J/K$$

$$W_{ex,1\to 2} = 39'000 - 293 * 45 = 25'815 \text{ J}$$

$$W_{lost} = W_{ex,1\to 2} - W_{produced} = W_{ex,1\to 2} = 25'815 \text{ J}$$

Fraction of work lost for the heat produced: $\frac{W_{lost}}{\Delta H} = 66\%$

Problem 4

Can you plot the efficiencies of the Otto, Diesel and Brayton cycles as a function of compression ratios? For the Diesel cycle, also consider different expansion ratios. Based on this can you rate the different engines if they were to use the same compression ratio?

Solution :

We use the following formulas for efficiencies for each of the cycles examined:

Otto's cycle efficiency:

$$\eta = 1 - r_C^{1-k}$$

Diesel cycle efficiency:

$$\eta = 1 - \frac{1}{k}\frac{\left(\frac{1}{r_e}\right)^k - \left(\frac{1}{r_c}\right)^k}{\frac{1}{r_e} - \frac{1}{r_c}}$$

where r_e is the expansion ratio of the Diesel engine.

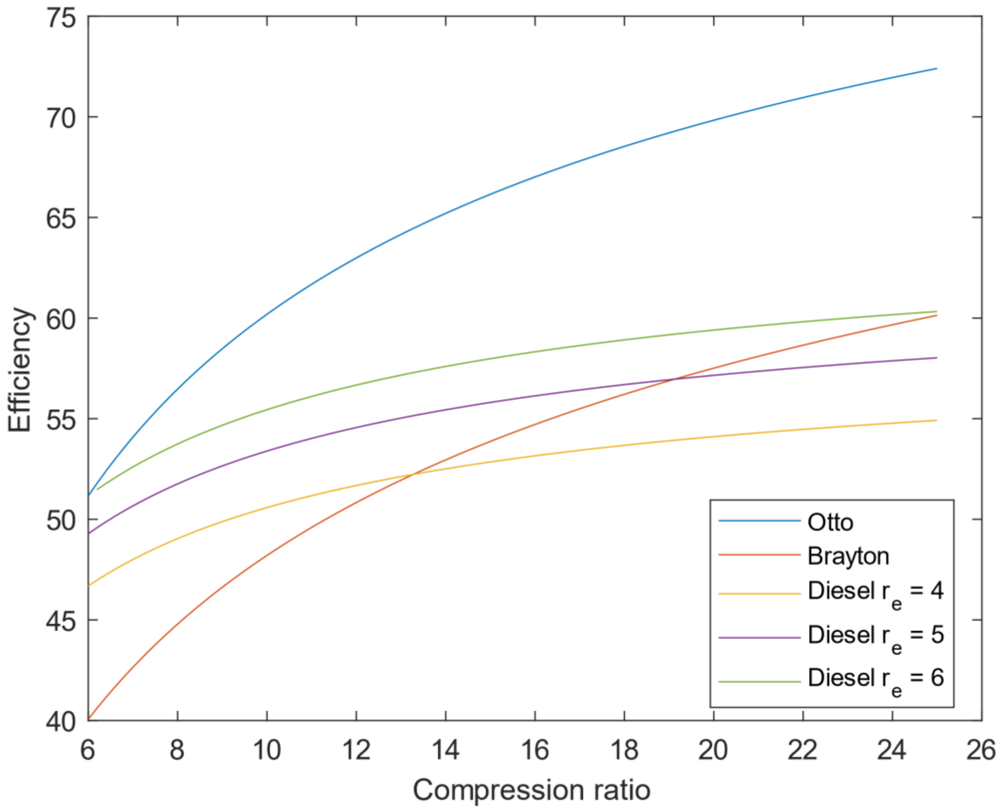
Efficiency of the Bryton cycle is given by equation (1.64) from the notes:

$$\eta = 1 - \left(\frac{P_A}{P_B}\right)^{\frac{k-1}{k}}$$

With $\frac{P_B}{P_A} = r_c$ it becomes

$$\eta = 1 - \left(\frac{P_A}{P_B}\right)^{\frac{k-1}{k}} = 1 - \left(\frac{1}{r_c}\right)^{\frac{k-1}{k}} = 1 - r_c{}^{-\frac{k-1}{k}}$$

On the figure bellow we have plotted efficiencies of different engines while varying the compression ratio.



The Otto's cycle is theoretically the most efficient cycle for all the compression ratios examined (6-25). However, we cannot compress gasoline above r_c~9 (with very high-octane fuel) due to its self-ignition. Therefore, the other two cycles (Brayton and Diesel) can effectively reach higher efficiencies. In addition, Diesel engines feature one more variable with is the expansion ratio (r_e). The more we are able to expand, the higher the efficiencies will be. Further, we notice that the Brayton's cycle efficiency varies the most with compression ratios. With lower compression ratios (<10) it is by far the least efficient solution, whereas when reaching high compression (>20) it becomes comparable or superior to Diesel engine efficiency (depending on how much we expand in the Diesel cycle).